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The Electrolytic Determination of Tin and Its Separation from Antimony with a Rotating Anode

THESIS

PRESENTED TO THE FACULTY OF PHILOSOPHY OF THE UNIVERSITY OF PENNSYLVANIA IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF PH. D.

BY

LUTHER FERREE WITMER

LANCASTER, PA.

1906

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The Electrolytic Determination of Tin and Its Separation from Antimony with the Use of a Rotating Anode

Tin has been made the subject of numerous investigations looking to its determination in the analytical way with the help of the electric current. Luckow[1] allowed the current to act on solutions of stannous and stannic chlorides in hydrochloric acid and found that the tin was completely deposited on the cathode as the white metal. He also precipitated tin from its alkaline solution (presumably ammonium sulphide) but when dissolved in sodium or potassium hydrates the precipitation was incomplete.

Wolcott Gibbs[2] in 1880 announced that he had deposited tin in mercury when the latter metal was made the cathode in an electrolytic cell.

Classen and von Reiss[3] in 1881 confirmed the statements made by Luckow and added that ammonium oxalate was a very good electrolyte from which to deposit tin. However if potassium oxalate was used a white basic salt was precipitated which could not be redissolved and precipitated on the dish.

They gave a number of quantitative determinations of this metal from a hydrochloric acid solution. Later Classen precipitated tin quantitatively from its ammonium oxalate double salt and also from a dilute solution of its ammonium sulpho salt. From dilute solutions of the sodium or potassium sulpho salts the precipitation was incomplete and from concentrated solutions of the sodium salt there was no precipitation. He therefore recommended that when these salts were present they should be transposed with ammonium sulphate

[1] Z. anal. Ch. 19, 13.
[2] Ch. News, 42, 291.
[3] Ber. 14,, 1622.

and the tin then precipitated from the ammonium sulphide solution. (See Smith's "Electrochemical Analysis," p. 113.)

Carl Engels[1] precipitated tin from a solution containing hydroxylamine hydrochloride or sulphate, ammonium acetate and tartaric acid.

Exner[2] working in this laboratory first made use of the rotating anode in the electroanalysis of tin solutions. He used 100 cc. of a hot concentrated solution of ammonium oxalate as the electrolyte and with a current of N. $D._{100} = 5$ amperes and a pressure of 5 volts was able to precipitate over .5 gram of tin in thirteen minutes.

Within the last year Miss Kollock[3], also working in this laboratory, deposited tin from a sulphuric acid solution using a rotating anode and a mercury cathode. She was able to deposit .4 gram of metal in 6 minutes or .8 gram in 9 minutes.

The rotating anode has never been applied to the precipitation of tin from an ammonium sulphide solution. It was to make a study of the rapid precipitation of the metal from this electrolyte that the present investigation was undertaken From the work done there is reason to believe that ammonium sulphide furnishes the best electrolyte for the precipitation of tin because of the splendid character of the deposits and also because a solution of this kind is very frequently met with in the general course of analysis. Free use has been made of all the available literature upon the subject and of Smith's "Electrochemical Analysis."

EXPERIMENTAL PART.

The solution of tin used in this work was one of stannic chloride dissolved in water to which had been added enough hydrochloric acid to prevent the precipitation of stannic hydrate. The stannic chloride was prepared in the usual way by passing chlorine gas over fused tin and then fractionating the liquid thus obtained. The distillation was repeated four

[1] Z. f. Elektrochem., 2, 418
[2] J. Am. Chem. Soc., 25, 896.
[3] J. Am. Chem. Soc., 27, 1532.

times and, after discarding the first portion, that coming over at 114° was collected allowing a considerable amount to remain in the distilling bulb. The liquid obtained was perfectly colorless and contained no iron. The solution of stannous ammonium chloride used in the first series of determinations was made by precipitating a large quantity, several grams, of tin from an ammonium oxalate solution, dissolving the deposit in hydrochloric acid and adding the calculated amount of ammonium chloride. The solution was evaporated to get rid of the large excess of acid and then diluted to a definite volume. In making a determination 10 cc. of this solution were pipetted out and allowed to flow into the ammonium sulphide contained in the platinum dish.

The ammonium sulphide was prepared by the usual method of saturating an ammonium hydroxide solution of specific gravity 0.94 with hydrogen sulphide gas and then adding an equal volume of hydrate. The sulphide thus obtained had a specific gravity of 0.985 and contained a small quantity of polysulphide which colored it slightly yellow.

The deposits were made on a platinum dish within which rotated a platinum spiral as described by Exner.[1] As remarked above when making a determination the ammonium sulphide was measured into the dish and the tin solution allowed to flow into it from the pipette. Enough water was then added to make the volume of the solution in the dish about 100 cc. The water in the first determinations was introduced cold but in the later ones it was heated to boiling. The anode was then started rotating after covering the dish with cover glasses and the current turned on. Sulphur always separated on the anode but on account of the agitation did not fall off and adhere to the deposit as reported by Classen who used a stationary anode. As the electrolysis continued the solution became less and less colored, due to the oxidation of the sulphur and in frequent instances when syphoned off was perfectly colorless although there were some few specks of sulphur floating around in it. When an insufficient quantity of sulphide was used the sulphur

[1] Loc. cit.

was completely oxidized and then an odor of chlorine could be detected, showing that the ammonium chloride was being decomposed. In this case there was liable to be a slight precipitate in the solution syphoned off.

The deposits were washed with hot water and then with absolute alcohol and ether and dried by the heat of the hand and gentle blowing. The dish was then wiped with a clean cloth and allowed to come to the temperature of the balance room before weighing. They were dissolved off the dish in hydrochloric acid, although in the later work with antimony it was found that a much quicker way to remove them was to treat with a solution of nitric and tartaric acids followed sometimes after rinsing with water by hydrochloric acid. In every case a dark stain was left on the dish which was removed by fusion with potassium bisulphate without any loss in weight by the dish. At first it was thought that the stain might be caused by some impurity in the sulphide but on passing hydrogen sulphide through a water solution of the bisulphate fusion a precipitate of stannous sulphide was thrown down.

The first attempts to deposit the metal were made using a solution of stannous ammonium chloride dissolved in ammonium sulphide. The results were as follows:

TABLE I.

No.	Sulphide.	Current, amperes.	Volts.	Time, min.	Tin present, grams.	Tin found, grams.
1	An excess	5.4	7	10	.1357	.1052
2	An excess	4	7.5	20	.1357	.1350
3	An excess	4	7.5	20	.1357	.1354
4	7 cc.	4.5	8	25	.1357	.1358
5	7 cc.	4–3	8–7	22	.1357	.1357
6	14 cc.	5.4–3	7–5.5	25	.2714	.2717
7	7 cc.	5–3	8–7	15	.1357	.1257

In numbers 1, 2, 4 and 7 the deposits looked almost like polished silver and remained perfectly bright even when rinsed with ammonium sulphide. Numbers 3 and 5 were rather dark colored for some unknown reason. In number 6 the acid of the tin solution was neutralized with a little ammonium hydrate and the precipitate then dissolved in ammonium sulphide.

The solution syphoned off from this and also that from numbers 2, 3, 4, 5 and 6 above showed no trace of tin sulphide when acidified with hydrochloric acid. The results show that over .13 gram of tin can be precipitated from its ammonium sulphide solution in 20 minutes and over .25 gram in 25 minutes and the character of the deposits was such that no sulphur or moisture could possibly be occluded by them.

A solution of stannic chloride was then prepared according to the directions given and a number of determinations made in which the amount of sulphide and strength of current were varied somewhat. An effort was made to obtain conditions which would give good deposits of larger amounts of tin in a shorter time.

TABLE II.

No.	Sulphide.	Current, amperes.	Volts.	Time, min.	Tin present, grams.	Tin found, grams.
1	20 cc.	5	8–7	20	.1946	.1932
2	20 cc.	6	8.5	25	.1946	.1943
3	20 cc.	11–8	11	15	.1946	.1944
4	15 cc.	5.5	9	20	.1946	.1949
5	10 cc.	5	9	20	.1946	.1946
6	8 cc.	5	11	15	.1946	.1903

The deposits above were all slightly crystalline but perfectly adherent. The solution syphoned off from numbers 2, 3, 4 and 5 gave no test for tin. Number 2 was electrolyzed for the first three minutes at 4 volts and 2 amperes, thinking the low current at the beginning would help to give a better deposit. The best conditions for .2 gram of metal are 15–20 cc. of sulphide and a current of 5.5 amperes and 9 volts.

Numerous other attempts were made to improve the character of the deposit. It was hoped that conditions could be found which would give the silver-white, bright and smooth deposits for larger amounts of tin. As the conditions in numbers 5 and 6 above had given better deposits than the others it was thought that probably a smaller amount of sulphide would give the required results. This was tried as low as 5cc. of sulphide being used for .2 gram of tin, but without success. The resistance of the electrolyte was greatly increased, but the

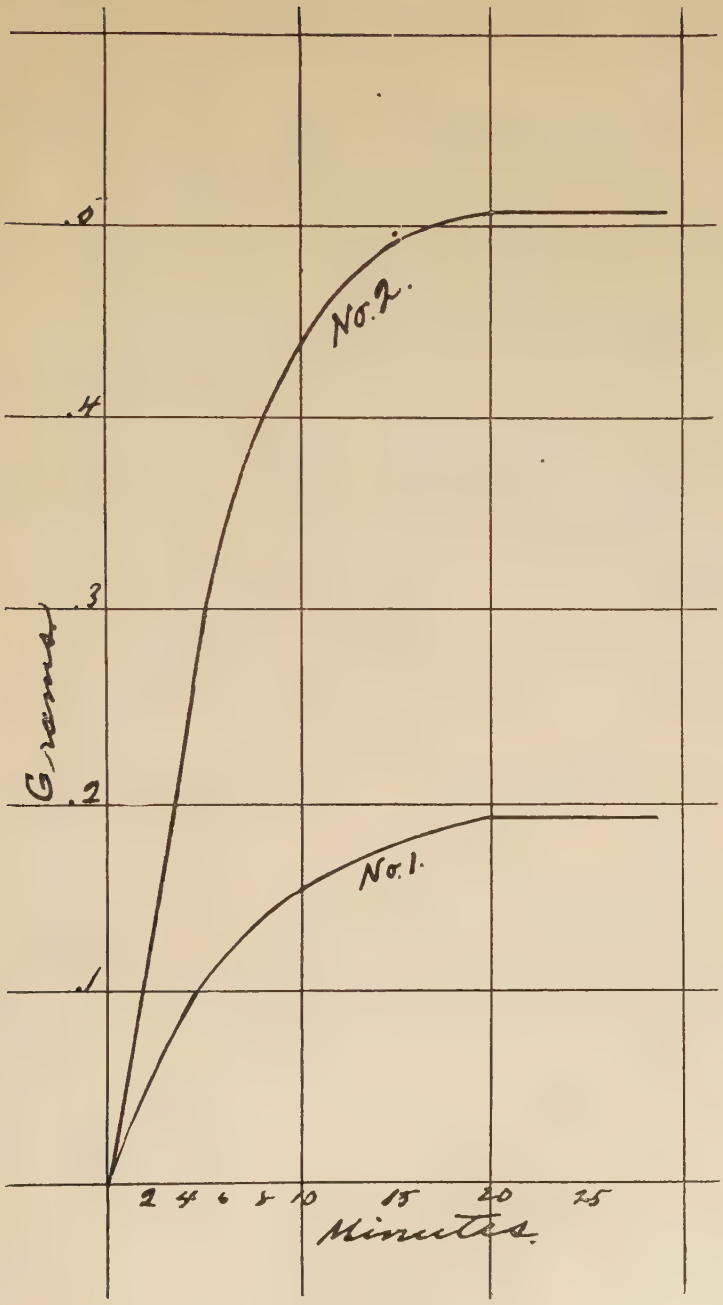
tin was not all precipitated in 20 minutes with a current of 5 amperes and 20 volts. The sulphide was so rapidly oxidized that before long the odor of chlorine could be detected. When the high pressures were used, a dark film remained on the dish after dissolving the deposit in hydrochloric acid. This could be rubbed off by the finger but when the voltage dropped as low as 10 the film was no longer noticed. When larger amounts up to .4 gram were precipitated the deposits were beautifully crystalline and perfectly adherent. It was thought that a reduction of the speed of rotation would have a beneficial effect and the number of revolutions was reduced to 250 per minute. It was at first thought that this was beneficial but later results have shown that the speed of rotation has little or no effect on the character of the deposit.

With a view to preparing time curves another solution of nearly the same strength as that used for the determinations in Table II was made up. The amount of tin in 10 cc. of this solution was determined as shown by the results in the first part of the table below. The rate at which that amount of metal deposited was then determined and a curve (No. 1) drawn.

TABLE III.

No.	Sulphide, in cc.	Current, amperes.	Volts.	Time, min.	Tin found, grams.
1	14	5	10	20	.1935
2	14	5	10	25	.1936
3	14	5	10	18	.1924
4	14	5	10	20	.1938
5	14	5	10	20	.1939
6	14	5	10	20	.1934
7	14	5	10	1	.0225
8	14	5	10	2	.0450
9	14	5	10	3	.0707
10	14	5	10	4	.0928
11	14	5	10	5	.1083
12	14	5	10	10	.1564
13	14	5	10	15	.1840
14	14	5	10	20	.1937

Of these deposits all those containing .1840 gram of tin or less were bright, silver-white in color. Above this amount they were finely crystalline. The curve shows that the rate



RATE OF DEPOSITION OF TIN.

of precipitation is almost constant for the first five minutes and then begins to decrease more and more rapidly. The rate of deposition is not as rapid in the first few minutes as has been noticed with other metals but this can easily be accounted for by the fact that the electrolyte was not first heated because of the volatility of the ammonium sulphide. Another reason to account for this will be referred to later.

Another series of analyses were made in which a larger quantity of metal was deposited and the rate of precipitation of this amount was also determined and the curve (No.2) drawn.

TABLE IV.

No.	Sulphide, in cc.	Current, amperes.	Volts.	Time, min.	Tin found, grams.
1	25	5	7·5	30	.5069
2	25	5	8	30	.5067
3	20	5	9	30	.5070
4	20	5	9	20	.5067
5	20	5	9	20	.5064
6	20	5	9	20	.5070
7	15	5	10	25	.5069
8	20	5	9	1	.0704
9	20	5	9	2	.1276
10	20	5	9	3	.1922
11	20	5	9	4	.2475
12	20	5	9	5	.2927
13	20	5	9	10	.4706
14	20	5	9	15	.4917
15	20	5	9	20	.5070

In number 1 of the above series the water added was heated to about 40° but in all the others it was heated to boiling and then added to the solution in the dish. In no case was the sulphide solution heated in the dish as this seemed to effect the smoothness of the deposit. All the deposits of .5 gram were light gray in color and very finely crystalline. Those of smaller amounts were silver-white. The solution syphoned off showed no trace of tin sulphide when acidified. The speed of rotation was 350 400 revolutions per minute. The time curve showed a very rapid precipitation for the first 10 minutes and then a rapid falling off during the deposition of the last traces.

It was then tried to deposit 1 gram of the metal from this

electrolyte. 30 cc. of ammonium sulphide were added to the solution, containing 1.0138 grams of tin, and this was electrolyzed for 30 minutes with a current of N. $D_{100} = 5$ amperes and 9 volts. The results were always too high. The deposits were spongy, but adherent. Thinking that they might have occluded water, one of them was heated in an oven to a temperature of 150°–160° for 1 hour, but the loss in weight was practically nothing. This occurence suggested the idea that possibly some of the crystalline deposits of lower weight might have occluded something. To determine whether this was the case a number of determinations were made, starting with a small quantity of metal which gave a bright, smooth silver-white deposit, which could not have occluded any moisture and doubling the quantity each time, using the same pipette in measuring out the solution.

TABLE V.

No.	Sulphide, in cc.	Current, amperes.	Volts.	Time, min.	Tin present, grams.	Tin found, grams.
1	15	5	11	25	—	.2038
2	20	5	9	25	.4076	.4077
3	20	5	9	25	.6114	.6118
4	21	5	9	25	.8152	.8152
5	25	5	9	25	1.0190	1.0235
6	25	5	9	25	1.0190	1.0216
7	25	5	8	30	1.0190	1.0232

The deposit in number 1 was bright and smooth, the others were crystalline but perfectly adherent. The solution syphoned off gave no test for tin. Up to .8 gram, therefore, nothing was occluded, but above that they were always too heavy. Number 5 was washed with carbon bisulphide to remove sulphur but the weight did not decrease.

In the later work on antimony it was attempted to deposit tin from a solution of ammonium sulphide, saturated with sulphur, with the expectation that the tin would come down and not the antimony. This expectation was not realized. Using a current of N. $D_{100} = 5$ amperes and 12 volts, no tin at all was deposited in the first 18 minutes. If the current was lowered after the tin began to deposit, it dissolved off again,

showing that a large excess of polysulphide completely prevented the precipitation of tin, which only takes place after most of the sulphur has been oxidized or eliminated from the solution by the action of the current. This may also have some bearing on the slow rate of precipitation, noticed when only small quantities of tin are being deposited, the proportion of polysulphides to the tin present being relatively greater.

CONCLUSION.

Tin can be precipitated from an ammonium sulphide electrolyte with a rotating anode in a perfectly adherent form. For amounts of tin less than 1 gram the precipitation is complete in 20–25 minutes, and no sulphur or moisture is occluded by the separated metal. When the electrolyte is heated, the rate of deposition is considerably increased. Polysulphides retard the precipitation, and, therefore, the amount of these present should be as small as possible.

SEPARATION OF ANTIMONY AND TIN.

Because of the difficulties attending the separation of antimony and tin in the ordinary methods of gravimetric analysis several attempts have been made to find an electrolytic method of separation. Luckow reported that in a solution of a mixture of chlorides of arsenic antimony and tin, the arsenic comes down first, then the antimony, and lastly the tin.

Alexander Classen dissolved the sulphides of antimony and tin in 80 cc. of a solution of sodium sulphide of specific gravity 1.13–1.15 to which were added two grams of sodium hydroxide. When this was electrolyzed the antimony was precipitated in two hours. The sulphide solution was then transposed with ammonium sulphate and electrolyzed for the tin[1].

Ost and Klapproth found that using concentrated solutions of sodium sulphide and a low pressure the antimony would not precipitate while with high pressures some of the antimony wandered to the anode as the complex on SbS_4. They therefore, used a diaphragm.[1]

[1] See Smith's "Electrochemical Analysis," p. 177.

In 1903 in this laboratory Exner,[1] using a rotating anode, deposited antimony from an electrolyte composed of sodium hydrogen sulphide, sodium hydrate and potassium cyanide. The object of the cyanide was to take up the excess of sulphur and prevent the formation of polysulphides, which were thought to be injurious to the deposit.

Within the last year Miss Langness[2] also working in this laboratory, succeeded in obtaining excellent deposits of antimony from an electrolyte, containing only sodium sulphide and potassium cyanide. In fact, she found that the addition of sodium hydrate was entirely unnecessary and that when the amount was increased to 1 gram it worked positive harm, making the deposits black, powdery and non-adherent. Miss Langness also used this electrolyte for separating arsenic and antimony, which was accomplished very readily.

These facts suggested the use of this same electrolyte for the separation of antimony and tin.

Accordingly, a solution of sodium sulphide was made up by saturating one half of a solution of sodium hydrate with hydrogen sulphide gas and then adding the other half. The solution was then filtered and evaporated rapidly to crystallization. The separated crystals were recrystallized from distilled water and then the crystals dissolved in water and the solution made of 1.18 specific gravity.

The antimony solution was prepared by dissolving antimonious oxide in an excess of sodium sulphide, filtering the solution and making up to a definite volume so that 10 cc. of the solution equaled approximately .1 gram of antimony.

The tin solution used was one of stannic chloride in hydrochloric acid, the same as that used in the work with tin. The antimony solution was pipetted into the platinum dish. The sulphide and cyanide were measured out and heated to boiling in a beaker glass. The proportion of cyanide to sulphide was the same as that used by Miss Langness in the determination of antimony. The tin solution was allowed to flow from the

[1] J. Am. Chem. Soc., 25, 896.
[2] J. Am. Chem. Soc., 27, 1524.

pipette into the hot sulphide solution, and this was then added to the antimony solution in the dish and the whole electrolyzed. The apparatus used was the same as that for tin and the deposits were washed and dried in the same way.

The first determinations made with the solutions given above, were not successful. The deposits were black, and powdery and pealed off the dish during the washing. From 15–20 cc. of sulphide were used and 2–4 grams of cyanide. The current was 3–4 amperes and 4–5 volts. It was thought that in spite of the precautions taken, there may have been sufficient hydrate present to cause the trouble, or that there had been impurities in the oxide. Accordingly, a new solution of antimony in sodium sulphide was made up, using the chloride. Fresh sodium sulphide was also prepared by saturating the hydrate with hydrogen sulphide until on stoppering the flask and shaking, no vacuum was formed. The antimony content of 10 cc. of the new solution was determined, according to the directions given by Miss Langness, and found to be 0.0929. A great many attempts were made to separate the antimony and tin, using this solution. The amount of tin present was 0.2038 gram.

TABLE VI.

No.	Na_2S spg. 1.18 in cc.	KCN grams.	Current, amp.	Volts.	Time, min.	Dilution, in cc.	Sb taken, grams.	Sb found, grams.
1	40	4	6	5	25	80	—	—
2	40	4	3	3	15	100	.0929	.0937
3	50	5	2.7	3	20	100	.0929	.0875
4	40	4	2.6	3	30	80	.0929	.0943
5	40	4	2.2	2.8	60	80	.0929	.0948
6	40	4	2.5	2.9	30	90	.1858	.1862
7	40	4	2.5	3	40	90	.1858	.1875
8	40	4	6	5	22	90	.1858	.1898
9	40 spg. 1. 2. 3	4	5	4	30	90	.1858	.1859

The results in Table VI were selected to show as nearly as possible the different conditions employed. The deposits were very good, being dark gray in color, perfectly smooth, and had a blue tinge, like metallic lead. Number one shows that under those conditions tin alone is not precipitated in the first 25 minutes. However, when the current was allowed to act 10

minutes longer, .0025 gram of tin was deposited. In number two, 20 cc. of water were added to the sulphide solution, but when thus diluted, tin was precipitated in 15 minutes. In number three where the sulphide was very concentrated the antimony was not all out in 20 minutes. When the time was lengthened tin was precipitated, although the amount deposited remained practically the same, when a slightly lower current was continued for one hour. The amount of antimony was then doubled, and the result showed that very probably all the antimony had been precipitated free from tin, but this proved to have been due to the fact that the determination was stopped just at the right time, as the next one showed, thus spoiling its usefulness for analytical purposes. In the last experiment, a solution of sodium sulphide of still higher specific gravity was used and the amount of antimony deposited was very close to the amount contained in the solution. All those deposits, which did not weigh heavier than the amount of antimony contained in the solution, gave no test for tin. All these results showed that all the antimony was precipitated before the tin began to come down, and that there was a short period after all the antimony was down, when no metal was deposited. It was to discover a means of knowing when this happened, and to extend its limits, if possible, that all the subsequent work was done.

The employment of sodium hydrogen sulphide, instead of sodium sulphide, suggested itself as it is more quickly prepared and possesses the additional advantage of readily dissolving stannous sulphide. This was tried, using the same quantities of potassium cyanide as had been used with the neutral sodium sulphide. The specific gravity of this sulphide ranged from 1.14–1.25, the other conditions remaining the same as before. The deposits were lighter in color and more metallic-looking, but were no more concordant than before. This electrolyte was also tried when the solution contained antimony alone, and some very fair results were obtained, but it was found that even when the antimony was all precipitated, a brown precipitate came down when hydrochloric acid was added to

the solution syphoned off, and this was darker when the current acted longer. The platinum dish lost about 1 milligram for each determination and it was supposed that the brown precipitate was platinum sulphide. This electrolyte was therefore, abandoned.

The sodium sulphide and potassium cyanide electrolyte were used, and a number of determinations made in which the pressure was lowered toward the end.

TABLE VII.

No.	Na_2S spg. 1.18, in cc.	KCN, grams.	Current, amp.	Volts.	Time, min.	Sn present, grams.	Sb present, grams.	Sb found grams.
1	50	5	4 3	3.5 3.2	15 5	.19	.1264	.1251
2	50	5.5	4 3	3.8 3.2	15 8	.19	.1264	.1252
3	50	5.5	4 3	3.8 3.3	15 15	.19	.1264	.1279
4	50	5	4 3 1	3.7 3.3 2.2	15 5 5	.19	.1264	.1277
5	50	5.5	4 3	3.8 3.3	15 6	.19	.1264	.1263
6	50	5.5	4 3 1	3.8 3.2 2.1	15 5 5	.19	.1264	.1272
7	50	5.5	4 3 1	3.8 3.2 2.2	15 5 2	.19	.1264	.1263
8	50	5.5	4 3 1	3.8 3.2 2.1	15 5 1	.19	.1264	.1258
9	50	5.5	4 3 1	3.8 3.2 2.1	15 5 10	.19	.1264	.1283
10	70 spg 1.20	7	4 3 1	3.6 3 1.8	15 5 10	.19	.1264	.1256

The deposits in all these were very good. However, as can be seen from experiments, 3, 4, 6 and 9, lowering the current toward the end is not effective in keeping up traces of tin. Hence, the results obtained in numbers 5, 7 and 8 could have very little analytical value. The conditions in number 10 were abandoned, because the antimony could not all be precipitated in 30 minutes and no especial advantage was seen in the large amounts of sulphide and cyanide used.

During all this time the platinum dish had lost regularly .8 milligram for each determination. The solution syphoned off was always yellow, showing the presence of polysulphides. A determination was tried omitting the cyanide and the deposit obtained was just as good as when cyanide was added. Under these new conditions a number of determinations were made and gave some very satisfactory results.

TABLE VIII.

No.	Na_2S spg. 1.18, in cc.	Dil., in cc.	Current, amp.	Volts.	Time, min.	Sn present, grams.	Sb present, grams.	Sb found, grams.
1	50	95	4	3.8	25	.19	.1264	.1260
2	50	95	4	3.8	26	.19	.1264	.1266
3	50	95	4	3.8	25	.19	.1264	.1252
4	50	95	5	4.2	25	.19	.1264	.1256
5	50	95	7	5	25	.19	.1264	.1269
6	50	95	7	5	15	.19	.1264	.1234
7	50	95	7	5	20	.19	.1264	.1262
8	50	105	7	5	30	.19	.2528	.2527
9	50	95	7	5.5	21	.19	.1264	.1280
10	50	95	7	5	20	.19	.1264	.1278
11	50	70	7	5	25	.19	.1264	.1354
12	50	95	5	4	25	.19	.1264	.1259
13	50	95	5	4	25	.19	.1264	.1259
14	50	95	5	4	30	.19	.1264	.1265

These deposits were all very good and for the most part contained no tin. However, in number 11 the tin was plainly visible, having been thrown down on top of the antimony. This did not have the characteristic blue color of antimony.

One determination of antimony alone was made, using 20cc. of a sodium sulphide solution specific gravity 1.18. The solution contained .1264 gram of antimony. With a current of 5 amperes and 4.7 volts for 25 minutes, the deposit, which was like the others, weighed 0,1260 gram.

After the determinations given above in Table VIII were made, a new stock of sulphide was prepared, and from that time on, except in a few instances, it was impossible to obtain deposits of antimony free from tin. Larger amounts of sulphide were used with greater or less concentration. Different amounts of sulphide were made up. The pressure of the electrolyte was varied by increasing the anode surface, but it was noticed that when the pressure fell below two volts the

deposit became black and began to dissolve off. It was then thought that the small amount of polysulphides in the solution held up the tin, and a rapid stream of hydrogen sulphide gas was passed into the sulphide solution for one half hour. When this sulphide was used, tin came down with the antimony. It was then thought to accomplish this same end by mixing the sodium sulphide solution with different amounts of sodium hydrogen sulphide solution of the same specific gravity, which had stood for some time. At first this seemed to do very well, giving deposits of antimony which were free from tin, but later, it was found that when the current acted for a longer time, a black border appeared around the top of the deposit and the antimony began to dissolve off. Fifteen or twenty minutes after the start the electrolyte became clear reddish in color and ceased to bubble. Apparently no action was taking place. Shortly after this the black ring appeared and crept farther and farther down the sides of the dish, leaving the platinum clean. This showed that a large excess of polysulphides prevented the complete precipitation of the antimony. Numerous attempts to prepare a sulphide, lying between this and the neutral sulphide, which must have been the case with that used in the determinations in Table VIII, were unsuccessful. Besides, with apparently identical conditions the results were not concordant. The amount of tin present was .1088 gram.

TABLE IX.

No.	Na_2S spg. 1.18, in cc.	NaSH spg. 1.18, in cc.	Current, amp.	Volts.	Time, min.	Dil. in cc.	Sb present, grams.	Sb found, grams.
1	45	7	4.8	4.2	40	85	.1064	.1061
2	45	7	4.8	4.2	40	85	.1064	.1021
3	45	6	5	4.3	40	85	.1064	.1064
4	45	6	5	4	40	85	.1064	.1016
5	45	6	5	4.2	40	85	.1064	.1056
6	45	6	5	4.2	36	85	.1064	.1052
7	45	6	5	4.2	40	85	.1064	.1033

The deposits in this series were fairly good, but in most cases the antimony began to dissolve off before all of it had been precipitated. At first it was thought that there was grease on the dish, but after thoroughly cleaning and igniting it the

deposits still did not reach to the edge of the solution, and it was concluded that the antimony dissolved in the polysulphide solution. When a small amount of potassium cyanide was added to the solution after it had cleared, the antimony began to deposit again, and a number of determinations were tried, using cyanide again in small quantities, but without any definite results.

CONCLUSION.

From the work done it is evident that three facts have been established: 1. Tin is not precipitated from solutions of sodium sulphide, containing large amounts of polysulphide. 2. Antimony is precipitated but not completely. 3. Between the concentration of polysulphides used in the last determinations and the neutral sulphide, there lies a point where all the antimony can be deposited free from tin. However, a method for preparing sulphide solution of this concentration has not been found, and lack of time has prevented further investigation of this subject.

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